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Synthesis of 1,3-diazabicyclo[3.1.0]hex-3-ene system under microwave irradiation

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Abstract

An efficient and straightforward approach for the three-component synthesis of 1,3-diazabicyclo[3.1.0]hex-3-enes from available aldehydes, premade Ketoaziridine and ammonium acetate under microwave irradiation and solvent free conditions is reported. The synthesized compounds showed good photochromic behaviour in crystalline and solution state.

Keywords: 1,3-Diazabicyclo[3.1.0]hex-3-ene; One-pot synthesis; Photochromic; Ketoaziridine

1. Introduction

Aziridines are valuable and multipurpose synthetic intermediates for the synthesis of a variety of nitrogen-containing functional compounds [1–3]. Aziridine ring is found in many natural products and exhibited significant activities such as antitumor, antibacterial, antifungal, and antibiotic [4]. Bicyclic aziridines primary due to the strained three-membered part, which experiences cleavage result of external factors have to be taken into consideration [5–36]. According to photochromism definition, *i.e.*, reversible colour change upon irradiation with UV light and having different absorption spectra [5–36], bicyclic aziridines exhibit this property. Bicyclic aziridines have been demonstrated to be very fascinating family of organic photochromic compounds having exclusive photochromic properties which create bistable molecules and undergo photochromism in the crystalline phase [9–36]. Some of the photochromic materials that show signs of photochromism in solid state include bicyclic aziridines [36], dithienylethenes [37], biindenylidenedione [38], hexaarylbiimidazoles [39], *N*-salicylideneanilines [40,41], spiropyrans [42], spirooxazines [43], dihydroindolizines [44], fulgides [45], and 2-(2′-4′-dinitrobenzyl)pyridine (DNBP) [46]. Investigation of convenient methods for the preparation of bicyclic aziridine derivatives has thus fascinated significant consideration and few methods to prepare these compounds and their photochromic properties are known [9–36]. Also some of bicyclic aziridines applied for the detection of Sn^{II} and Sr^{II} in real samples [47–50]. Although several report to preparation of this compounds so far, to the best of our knowledge, no reports that including synthesis of bicyclic aziridines from ketoaziridine under microwave irradiation have been reported. In continuation of our studies on the synthesis of 1,3-diazabicyclo[3.1.0]hex-3-enes [12–21], and

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with regard to the applications of these attractive compounds, an effective, simple, and straightforward process to the preparation of 1,3-diazabicyclo[3.1.0]hex-3-enes **4** (**a**–**o**) under microwave conditions is presented in this report.

2. Experimental

Melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AVANCE DRX-500 MHz and 400 MHz using $CDCl_3$ or DMSO-d_6 as solvent. FT-IR spectra were recorded on a PerkinElmer RXI spectrometer. UV spectra were recorded using Analytik Jena UV/Vis spectrometer (Specord 205) or Perkin-Elmer Lambda spectrophotometer. The photoinduced (open) form **B** was formed upon UV irradiation (Hg lamp DRSh-260+ UV-transmitting glass filters). Chemicals were obtained from Merck and Fluka. The modified microwave oven [51] was used. The development of reactions was monitored by thin layer chromatography (TLC) on silica gel 60 GF_{254} aluminium sheets, using ethyl acetate: petroleum ether (1: 3) as mobile phase. The spots were exposed by UV light and iodine vapour.

2.1. General procedure for preparation of 1,3-diazabicyclo[3.1.0]hex-3-enes, *4* (*a*–*o*)

The mixture of ketoaziridine (1 mmol), aldehyde or ketone (1 mmol) and ammonium acetate (10 mmol) was heated under microwave irradiation for given time. The progress of the reaction was monitored by TLC. After completion of the reaction, after cooling to room temperature, the cold reaction mixture was treated with ethanol; solid products was filtered, dried and recrystallized from ethanol or purified by column chromatography to afford the title compounds. All title compounds except **4** (**l**–**m**), were known and are identified by comparison of their physical and spectroscopic data with those of authentic samples. Spectral data for some of the compounds as follows:

2,2-Dimethyl-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4a**)

As a colourless solid (closed form), which after irradiation with UV light converted to blue (open-form); UV–vis (EtOH) λ_{max}/nm: 286 before irradiation and 285, 405 after irradiation; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.62 (s, 3H), 1.63 (s, 3H), 2.63 (s, 1H), 3.63 (s, 1H), 7.46–7.53 (m, 5H), 7.88 (t, J = 1.1, 7.1 Hz, 2H), 8.23 (d, J = 8.6 Hz, 2H). IR (KBr) ν: 3050, 2980, 2920, 1600, 1570, 1510, 1440, 1340, 1220, 1100, 910, 860, 820, 760, 740, 690 cm^{-1}.

6-(4-Nitrophenyl)-4-phenyl-2,2-dipropyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4c**)

As a colourless solid (closed form), which after irradiation with UV light converted to blue (open-form); UV–vis (EtOH) λ_{max}/nm: 282 before irradiation and 282, 416 after irradiation; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.93–1.00 (tt, J = 7.0, 7.3 Hz, 6H), 1.30–1.36 (m, 1H), 1.51–1.60 (m, 2H), 1.65–1.67 (m, 2H), 1.89–1.93 (m, 3H), 2.65 (s, 1H), 3.54 (s, 1H), 7.46–7.54 (m, 5H), 7.89 (d, J = 7.5 Hz, 2H), 8.22 (d, J = 8.5 Hz, 2H). IR (KBr) ν: 3100, 3080, 2950, 2920, 2880, 1600, 1570, 1510, 1440, 1340, 1240, 1140, 960, 860, 830, 760,740, 690 cm^{-1}.

2-Isobutyl-2-methyl-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4d**)

As a colourless solid (closed form), which after irradiation with UV light converted to blue (open-form); UV–vis (EtOH) λ_{max}/nm: 281 before irradiation and 282, 402 after irradiation; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.02 (d, J = 6.6 Hz, 3H), 1.07 (d, J = 6.6 Hz, 3H), 1.57 (s, 3H), 1.78–1.87 (m, 2H), 1.94–1.98 (m, 1H), 2.64 (s, 1H), 3.52 (s, 1H), 7.44–7.53 (m, 5H), 7.87 (d, J = 7.4 Hz, 2H), 8.20 (d, J = 8.6 Hz, 2H); IR (KBr) ν: 3050, 2950, 2900, 2850, 1600, 1570, 1510, 1440, 1340, 1100, 940, 860, 760, 740, 695 cm^{-1}.

2-(4-Methoxyphenyl)-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4f**)

As a colourless solid (closed form), which after irradiation with UV light converted to violet (open-form); UV–vis (EtOH) λ_{max}/nm: 280 before irradiation and 283, 409 after irradiation; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.55 (s, 1H), 3.79 (s, 1H), 3.82 (s, 3H), 6.78 (s, 1H), 6.89 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 8.02 (d, J = 7.6 Hz, 2H), 8.19 (d, J = 8.4 Hz, 2H); IR (KBr) ν: 3050, 3000, 2950, 2850, 1600, 1570, 1520, 1510, 1440, 1340, 1250, 1170, 1030, 860, 790, 765, 740, 690 cm^{-1}.

6-(4-Nitrophenyl)-4-phenyl-2-(2,4,6-trimethylphenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**4g**)

As a colourless solid (closed form), which after irradiation with UV light converted to blue: (open-form); UV–vis (EtOH) λ_{max}/nm: 280 before irradiation and 281, 405 after irradiation; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.26 (s, 3H), 2.50 (s, 6H), 2.59 (s, 1H), 3.65 (s, 1H), 6.80 (s, 1H), 6.85 (s, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.52–7.58 (m, 3H), 8.02 (d, J = 7.1 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H); IR (KBr) ν: 3050, 2950, 2900, 2850, 1600, 1570, 1510, 1440, 1340, 1040, 1020, 960, 850, 760, 740, 690 cm^{-1}.

2-[(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)]phenol (**4h**)

As a colourless solid, which after irradiation with UV light converted to pale pinkish: UV–vis (EtOH) λ_{max}/nm: 208, 245, 262 (shoulder) before irradiation and 208, 272, 415 after irradiation; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.51 (s, 1H), 3.81 (s, 1H), 6.69 (s, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.42–7.46 (m, 4H), 7.53 (t, J = 7.5 Hz, 1H), 7.87 (d, J = 7.4 Hz, 2H), 8.16 (d, J = 8.6 Hz, 2H), 9.40 (s,1H); IR (KBr) ν: 3200–3050, 2850, 1600, 1580, 1510, 1480, 1440, 1340, 1240, 1050, 840, 740, 710, 690 cm^{-1}.

3-[(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)]phenol (**4i**)

As a colourless solid, which after irradiation with UV light converted to greenish blue: UV–vis (EtOH) λ_{max}/nm: 205, 236, 276 before irradiation and 205, 260, 410 after irradiation; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.49 (s, 1H), 3.48 (s, 1H), 6.41(s, 1H), 6.48 (dd, J = 2.0, 8.0 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 6.73 (s, 1H), 6.86 (t, J = 7.8 Hz, 1H), 7.15 (d, J = 8.7 Hz, 1H), 7.20 (t, J = 7.7 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 8.56 (s, 1H). IR (KBr) ν: 3250, 3080, 3010, 1605, 1580, 1510, 1485, 1440, 1340, 1295, 1220, 1040, 890, 860, 770, 760, 740, 690 cm^{-1}.

2-methoxy-4-[(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)]phenol (**4k**)

As a colourless solid, which after irradiation with UV light converted to deep blue: UV–vis (EtOH) λ_{max}/nm: 205, 254 before irradiation and 205, 262, 415 after irradiation.^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.55 (s, 1H), 3.79 (s, 1H), 3.84 (s, 3H), 6.73 (s, 1H), 6.87 (d, J = 8.2 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 7.10 (s, 1H), 7.42 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 7.3 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 8.02 (d, J = 7.3 Hz, 2H), 8.18 (d, J = 8.7 Hz, 2H); IR (KBr) ν: 3250, 3080, 2920, 2850, 1595, 1570, 1508, 1440, 1420, 1340, 1270, 1240, 1160, 1050, 960, 860, 840, 770, 740, 690 cm^{-1}.

6-(4-Nitrophenyl)-4-phenyl-2-(pyridin-2-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**4l**)

As a colourless solid (closed form), which after irradiation with UV light converted to green (open-form), m.p. 138–139 °C; UV–vis (EtOH) λ_{max}: 207, 258 nm before irradiation and 215, 275, 408 after irradiation; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.89 (s, 1H), 3.69 (s, 1H), 6.70 (s, 1H), 7.17 (m, 1H), 7.36 (d, J = 8.7 Hz, 2H), 7.43 (t, J = 7.6 Hz, 3H), 7.49 (t, J = 7.4 Hz, 1H), 7.64 (td, J = 7.7, 1.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 2H), 8.08 (d, J = 8.6 Hz, 2H), 8.58 (dd, J = 4.8, 0.6 Hz, 1H); IR (KBr) ν: 3080, 3000, 2900, 1600, 1585, 1518, 1450, 1438, 1340, 1320, 1050, 1040, 985, 800, 770, 750, 690 cm^{-1}.

6-(4-Nitrophenyl)-4-phenyl-2-(thiophen-3-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**4m**)

As a pale beige solid (closed form), which after irradiation with UV light converted to deep purple (open-form); UV–vis (EtOH) λ_{max}/nm: 245, 285 (shoulder) before irradiation, and 259, 415 after irradiation; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.54 (s, 1H), 3.78 (s, 1H), 6.74 (s, 1H), 7.23–7.24 (m, 1H), 7.33–7.35 (m, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.49–7.55 (m, 3H), 7.98 (d, J = 6.8 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ: 42.0, 57.6, 93.7, 122.9, 123.7, 126.4, 126.7, 127.3, 128.5, 128.9, 131.5, 131.9, 139.2, 145.4, 147.3, 170.4; IR (KBr) ν: 3060, 1600, 1510, 1445, 1340, 1015, 975, 865, 750, 700, 690 cm^{-1}.

6-(4-nitrophenyl)-4-phenyl-2-thiophen-2-yl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4n**)

As a colourless solid (closed form), which after irradiation with UV light converted to purple (open-form); UV–vis (EtOH) λ_{max}/nm: 285 before irradiation, and 289, 408 after irradiation; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.72 (s, 1H), 3.83 (s, 1H), 6.89 (s, 1H), 7.02 (t, J = 4.8, 3.7 Hz, 1H), 7.17 (d, J = 3.2, 1H), 7.29 (d, J = 5.2 Hz, 1H), 7.47 (d, J = 8.6 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.58 (t, J = 7.3 Hz, 1H), 8.01 (d, J = 7.4 Hz, 2H), 8.21 (J = 8.6 Hz, 2H), ^{13}C NMR ($CDCl_3$, 125 MHz): 42.9, 58.6, 93.5, 124.2, 126.1, 126.3, 127.5, 127.9, 129.1, 129.43, 131.8, 132.6, 140.9, 145.7, 147.9, 171.5; IR (KBr) ν: 3050, 1595, 1508, 1440, 1340, 1010, 970, 880, 790, 760, 740, 700, 690 cm^{-1}.

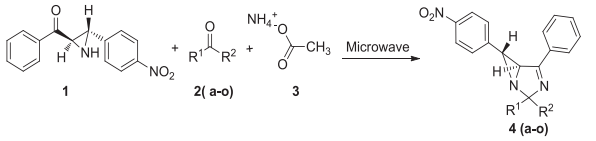
6-(4-nitrophenyl)-4-phenyl-2-furan-2-yl-1,3-diazabicyclo[3.1.0]hex-3-ene (**4o**)

As a colourless solid (closed form), which after irradiation with UV light converted to blue (open-form); UV–vis (EtOH) λ_{max}/nm: 290 before irradiation, and 295, 405 after irradiation; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.95 (s, 1H), 3.80 (s, 1H), 6.39 (dd, J = 1.6, 3.0 Hz, 1H), 6.66 (s, 1H), 7.45–7.59 (m, 6H), 7.97 (d, J = 7.3 Hz, 2H), 8.20 (d, J = 8.6 Hz, 2H); IR (KBr) ν: 3100, 3050, 2890, 1600, 1575, 1510, 1345, 1280, 1100, 740, 690 cm^{-1}.

3. Results and discussion

Bicyclic aziridines **4** (**a**–**o**) was synthesized from premade ketoaziridine compound **1** [12,52], and commercially aldehhydes or ketones **2**, in presence of ammonium acetate **3** (Scheme 1).

At first the reaction of ketoaziridine **1**, acetone and ammonium acetate under microwave irradiation was performed. **4a** was given in excellent yield and shorten time. Explore of ^{1}H NMR spectrum and physical data



Entry	Product (Yield %)	R^1	R^2	Time (min)	M.p (°C) Found	M.p (°C) Reported (Lit.)
1	**4a** (94)	Me	Me	1.5	183-184	182-183[25]
2	**4b** (93)	Et	Me	4	145-146	146-147[25]
3	**4c** (93)	pr	pr	5	137-138	136-137[12]
4	**4d** (92)	Me	^{i}Bu	5	148-149	147-148[12]
5	**4e** (96)	Ph	H	2.5	176-177	175-176[25]
6	**4f** (92)	4-MeOC_6H_4	H	5	162-163	162-163[19]
7	**4g** (75)	2,4,6-$Me_3C_6H_2$	H	10	163-164	162-163[19]
8	**4h** (88)	2-OHC_6H_4	H	7	166-167	167-168[15]
9	**4i** (90)	3-OHC_6H_4	H	6	172-173	171-172[15]
10	**4j** (91)	4-OHC_6H_4	H	5	181-183	180-181[15]
11	**4k** (85)	4-OH,3-MeOC_6H_3	H	7	188-189	189-190[15]
12	**4l** (90)	2-pyridyl	H	7	138-139	-
13	**4m** (94)	3-thienyl	H	4	175-176	-
14	**4n** (95)	2-thienyl	H	3	176-177	177-178[12]
15	**4o** (88)	furan-2-yl	H	5	168-170	169-170[13]

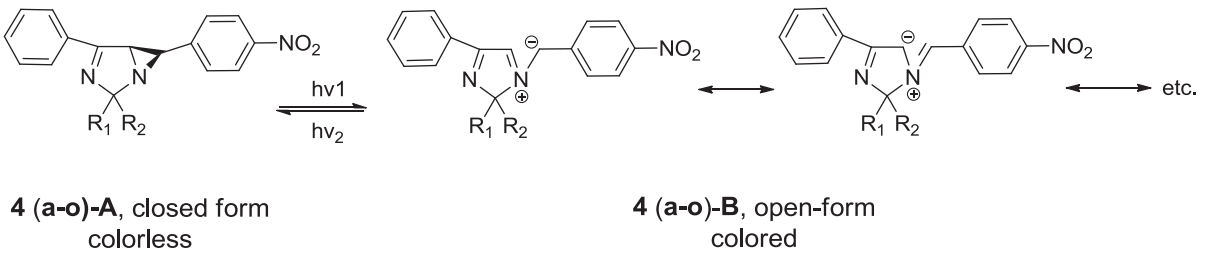
Scheme 1. Preparation of 1,3-diazabicyclo[3.1.0]hex-3-enes, **4** (**a**–**o**).

indicates formation of product. The ^{1}H NMR spectrum of this compound exhibite the two singlets signal at δ 1.62 and 1.63 ppm belonging to two methyl groups in C-2 position. The resonances of the two protons belong to H-5 and H-6 of the aziridine ring appeared at δ 3.63 and 2.63 ppm, respectively. The signals of the aromtic protons were displayed in the 8.23 ppm (as a doublet), 7.88 ppm (as a triplet), and region δ 7.46–7.53 ppm (as multiplets). The IR spectrum was devoid of the C=O and NH absorption bands at $\upsilon = 1660$ and 3330 cm^{-1} of the precursor (compound **1**). The presence of the absorption band at $\upsilon = 1600\ cm^{-1}$ confirmed formation of C=N bond. This result encouraged us to perform the other reactions with the aim to obtain the photochromic products. Reaction in microwave conditions resulted in higher yields and shorter reaction times than other conditions such as using solvent [9–36], also aromatic aldehydes relative to ketones are suitable for the reaction. Mostly utilized aldehydes or ketones are liquid (Scheme 1, entries 1–8 and 12–15), and in the other cases (Scheme 1, entries 9–12) 3–5 drops ethanol were used. It seems that, electronic and steric factors are influence reaction. When salicylaldehyde were reacted with ketoaziridine compound **1** and ammonium acetate **3**, corresponding product **4h** was produced in relatively lower yield, which may be due to the steric hindrance of the hydroxyl group. Also, such result was obtained, when 2,4,6-trimethylbenzaldehyde was used, that indicates steric factor.

All products **4** (**a**–**o**) were obtained as crystals after work-up and were confirmed by their physical and spectral data. For instance, the structures of compounds **4** were deduced from their IR, ^{1}H and ^{13}C NMR spectra data. The NMR spectra of synthesized compounds in $CDCl_3$ are showed signals at ambient temperature as expected. For instance, the ^{1}H NMR spectrum of **4m** showed three singlet signals for the H-2, H-5 and H-6 protons at δ 6.74, 3.78 and 2.54 ppm, respectively. The *ortho*- and *meta*-protons of *p*-nitrophenyl group appeared as two doublets at δ 8.20 and 7.44 ppm, respectively. The resonances of the two protons belong to *ortho*-protons of the phenyl ring appeared at δ 7.98 ppm as a doublet. Also, the ^{1}H NMR spectrum of **4 m** showed multiplet for the thiophen ring (δ 7.23–7.24 and δ 7.33–7.35 ppm). All the other aromatic protons were observed as multiplets in the region δ 7.49–7.55 ppm, integrating for three protons. The corresponding signals in the other compounds were appeared in the same region of the ^{1}H NMR spectra. The ^{13}C NMR spectrum of **4m** revealed 16 distinct resonances in agreement with the suggested structure. Signal appears at δ 93.7 ppm indicating the presence of carbon at C-2 position. Signals appeared at δ 57.6 and 42.0 ppm indicated the presence of aziridine ring carbons at 5- and 6-positions, respectively. The C=N resonance was visible at 170.4 ppm. The resonances of the other carbons were visible at δ 122.9–147.3 ppm. The NMR spectra of the other compounds **4** (**a**–**o**) are similar to those of **4m** except for the alkyl or aryl groups in C-2 position, which show, in each case, characteristic signal in appropriate regions of the spectra. It can be mentioned that formation of *endo*- and *exo*-isomers with orientation of substituent in C-2 position is possible. The ^{1}H NMR spectrum of purified compounds **4** are indicated that signals belong to only one stereoisomer. With consideration of chemical shifts for the H-2, H-5 and H-6 protons, and comparison with those obtained by reported in literature [9–36], *endo*-isomer is major compound.

The photochromic behaviour of 1,3-diazabicyclo[3.1.0]hex-3-enes is based on a reversible ring opening of aziridine moiety at the C–C bond stimulated by UV light, which transform a colourless form (closed-ring) to the coloured form (open-ring) (Scheme 2) [9–36].

According to UV/vis spectra, all target compounds **4** (**a**–**o**) showed good photochromic reaction. To search the photochromic behaviour of target compounds, the solution of material synthesized was exposed to 365 nm UV light for a given time at ambient temperature. For example, a solution of **4m** in EtOH is weakly coloured (**4m-A**-form). Upon irradiation at 365 nm to this solution, the closed form of **4m-A**-form was changed to the open form of **4m-B**-form; go along with by noticeable



Scheme 2. Proposed photochromic colour change of 1,3-diazabicyclo[3.1.0]hex-3-enes, **4** (**a**–**o**).

changes in the absorption spectra as shown in Fig. 1. As shown in Fig. 1, when **4m** was irradiated with UV light at 365 nm the colourless solution of **4m** turned gradually coloured and the new absorption bands appeared at 259 and 415 nm, which indicated that the zwitterionic species **4m-B** (open-ring form) was produced and exhibited photochromic behaviour. As expected, continuous irradiation time resulted in intensity the absorption band in the visible region is increased and in the ultraviolet is decreased. The same results were obtained for the other compounds. Colour change in solid and solution state was observed by eye-naked, when compounds exposed to light (UV light from mercury, xenon lamp, ordinary room light or sunlight). Similar results were also achieved when the other synthesized compounds were irradiated with UV light. It is noteworthy to mention that nitro group at *para*-position on phenyl ring in aziridine moiety is much more photochromic behaviour than chlorine group at *para*- or nitro at *meta*-position. This property attributed to π-conjugation for zwitterionic species, which possess nitro group at *para*-position.

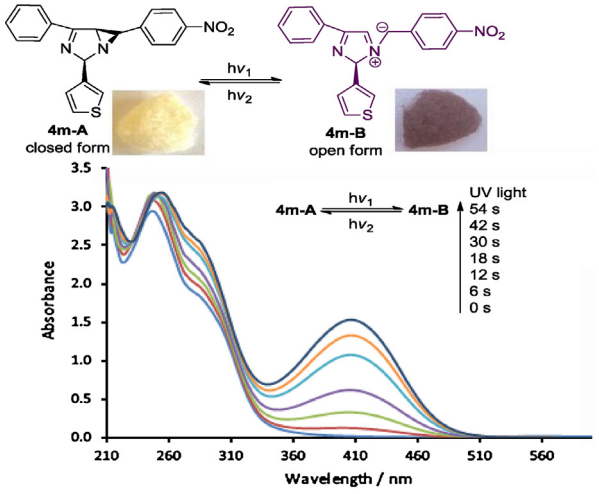


Fig. 1. Photochromic reaction (top) and UV/Vis spectral changes (bottom) of 4 m in EtOH (2.0×10^{-4} M) irradiation with 365 nm light, time irradiation from bottom to up: 0, 6, 12, 18, 30, 42, 54 s.

4. Conclusion

In summary, an efficient, facial and straightforward protocol for the three-component synthesis of 1,3-diazabicyclo[3.1.0]hex-3-enes in high yield have been established. The described method has advantages on short reaction time, simple work-up and ready achieve to derivatives of bicyclic aziridines. These compounds exhibit good photochromic behaviour in crystalline and solution state.

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References

[1] J.M. Concellón, P.L. Bernad, J.R. Suárez, Stereoselective functionalization of 2-(1-aminoalkyl)aziridines *via* lithiation of aziridine–borane complexes, Chemistry: A European Journal 11 (2005) 4492–4501.

[2] C. Gaebert, J.M. Mattay, Toubartez, S. Steenken, B. Muller, T. Bally, Radical cations of phenyl-substituted aziridines: what are the conditions for ring opening? Chemical European Journal 11 (2005) 1294–1304.

[3] A.F. Khlebnikov, M.S. Novikov, Fused aziridines as sources of azomethine ylides, Chemistry of Heterocyclic Compounds: A Series of Monographs 48 (2012) 179.

[4] J.C. Hegde, K.S. Girish, A. Adhikari, B. Kalluraya, Novel one-pot synthesis of aziridines carrying sydnone moiety and their biological study, Synthetic Communications 43 (2013) 301–308.

[5] H. Dürr, H. Bouas-Laurent, Photochromism: Molecules and Systems, Elsevier, Amsterdam, 2003.

[6] A.I. Zbruyev, F.G. Yaremenko, V.A. Chebanov, S.M. Desenko, O.V. Shishkin, E.V. Lukinova, I.V. Knyazeva, Synthesis and study of new 2-aryl-1-(4-nitrophenyl)-1,1a-dihydroazireno[1,2-*a*]quinoxaline derivatives, Russian Chemical Bulletin International Edition 55 (2006) 362–368.

[7] Z. Kaluski, E. Figas, N.P. Vorobyeva, V.D. Orlov, Crystal and molecular structure of 2-(4-methoxyphenyl)-4-phenyl-6-(4-nitrophenyl)-1,3-diazabicylo[3.1.0]hex-3-ene, Journal of Structural Chemistry 35 (1994) 134–137.

[8] A.I. Zbruev, V.D. Panikarskaya, N.A. Kasyan, L.N. Zavora, L.N. Lisetskii, S.M. Desenko, V.A. Chebanov, The photoinduced

transformations of aziridine derivatives in liquid crystalline matrices, Russian Journal of Physical Chemistry A 83 (2009) 1350–1354.

[9] G. Bruno, F. Nicol, A. Rotondo, F. Risitano, G. Grassi, F. Foti, Structure investigation of bridgehead aziridine: synthesis, theoretical, and crystallographic study of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene, Helvetica Chimica Acta 89 (2006) 190–200.

[10] V.V. Dyakonenko, A.V. Maleev, A.I. Zbruyev, V.A. Chebanov, S.M. Desenko, O.V. Shishkin, Layered crystal structure of bicyclic aziridines as revealed by analysis of intermolecular interactions energy, CrystEngComm 12 (2010) 1816–1823.

[11] F. Risitano, G. Grassi, F. Foti, S. Moraci, A novel efficient three-component one-pot synthesis of 1,3-diazabicyclo[3.1.0]hex-3-ene system under microwave irradiation, Synlett (2005) 1633–1635.

[12] N.O. Mahmoodi, H. Kiyani, Synthesis of thiophene derivatives of 1,3-diazabicyclo[3,1,0]hex-3-ene, Bulletin of the Korean Chemical Society 25 (2004) 1417–1420.

[13] N.O. Mahmoodi, M.R. Yazdanbakhsh, H. Kiyani, B. Sharifzadeh, Synthesis and photochromic properties of new heterocyclic derivatives of 1,3-diazabicyclo[3.1.0]hex-3-ene, Journal of the Chinese Chemical Society 54 (2007) 635–641.

[14] N.O. Mahmoodi, K. Tabatabaeian, A. Ghavidast, Synthesis and photochromic behavior of mono, and biphotochromic system linked by *p*-phenylene bridge, Chinese Chemical Letters 21 (2010) 1199–1202.

[15] H. Kiyani, N.O. Mahmoodi, K. Tabatabaeian, M.A. Zanjanchi, Synthesis and photochromism of 1,3-diazabicyclo[3.1.0]hex-3-ene phenol rings, Mendeleev Communications 19 (2009) 203–205.

[16] N.O. Mahmoodi, K. Tabatabaeian, H. Kiyani, Two 1,3-diazabicyclo[3.1.0]hex-3-enes with a 'tripod' core, Helvetica Chimica Acta 95 (2012) 536–542.

[17] H. Kiyani, N.O. Mahmoodi, K. Tabatabaeian, M.A. Zanjanchi, Photochromic behavior of several new synthesized bis-1,3-diazabicyclo[3.1.0]hex-3-enes, Journal of Physical Organic Chemistry 22 (2009) 559–567.

[18] N.O. Mahmoodi, E. Asadollahi, H. Kiyani, N. Naseri, Synthesis and photochromism of quinolines and benzo[h]quinolines of 1,3-diazabicyclo[3.1.0]hex-3-ene, International Journal of Photoenergy (2011) 6, Article ID 218427, doi:10.1155/2011/218427.

[19] N.O. Mahmoodi, H. Kiyani, K. Tabatabaeian, M.A. Zanjanchi, M. Arvand, B. Sharifzadeh, NMR structural elucidation and photochromic behavior of new derivatives 1,3-diazabicyclo[3.1.0]hex-3-ene, Russian Journal of Organic Chemistry 46 (2010) 884–889.

[20] N.O. Mahmoodi, M.A. Zanjanchi, H. Kiyani, Photochromism of several synthesised 1,3-diazabicyclo[3,1,0]hex-3-ene derivatives, Journal of Chemical Research 6 (2004) 438–440.

[21] Y. Zhu, S. Wang, S. Wen, P. Lu, Y. Wang, Copper-catalyzed cascade approach to 1,3-diazabicyclo[3.1.0]hex-3-enes from aziridines and ethyl diazoacetate, Tetrahedron Letters 51 (2010) 4763–4766.

[22] V.A. Chebanov, S.M. Desenko, T.W. Curley, Azaheterocycles Based on α,β-Unsaturated Carbonyls, Springer-Verlag, Berlin, Heidelberg, 2008, pp. 17–32, Chapter 1.

[23] A. Padwa, J. Smolanoff, S.I. Wetmore, Photocyclodimerization of arylazirenes to 1,3-diazabicyclo[3,1,0]hex-3-enes, Journal of the Chemical Society, Chemical Communications (7) (1972) 409–410.

[24] A. Padwa, S.I. Wetmore, Some thermal and photochemical reactions of *cis*- and *trans*-substituted enedi-imides, Journal of the Chemical Society, Chemical Communications (20) (1972) 1116–1117.

[25] H.W. Heine, H.R. Weese, R.B. Cooper, A.J. Durbetaki, X.V. Aziridines, The synthesis and reactions of 1,3-diazabicyclo[3.1.0]hex-3-enes, Journal of Organic Chemistry 32 (1967) 2708–2711.

[26] A. Padwa, M. Dharan, J. Smolanoff, S.I. Wetmore, Photochemical transformations of small ring heterocyclic compounds. XLVII. Electronic details of the photocycloaddition of arylazirines, Journal of the American Chemical Society 95 (1973) 1954–1961.

[27] A. Padwa, G. Edward, photochemical transformations of small ring heterocyclic compounds. XLII. Photochemical reorganizations in the 1,3-diazabicyclo[3.1.0]hex-3-ene system, Journal of the American Chemical Society 94 (1972) 7788–7797.

[28] A. Padwa, S. Clough, E. Glazer, Photochemical transformations of small-ring heterocyclic compounds. XXIV. Photoisomerization of the Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene system, Journal of the American Chemical Society 92 (1970) 1778–1779.

[29] V.V. Dyakonenko, O.V. Shishkin, A.V. Zbruev, S.M. Desenko, 2,2-Dimethyl-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene, Acta Crystallographica Section E Structure Reports Online E61 (2005) o667–o668.

[30] A. Padwa, E. Glazer, The effect of solvent on the photorearrangement of the 1,3-diazabicyclo[3,1,0]hex-3-ene system, Journal of Chemical Communications D (15) (1971) 838–839.

[31] A.M. Trozolo, T.M. Leslie, A.S. Sarportdar, R.D. Small, G.J. Ferraudi, T. DoMinh, R.L. Hartless, Photochemistry of some three-membered heterocycles, Pure and Applied Chemistry 51 (1979) 261–270.

[32] A.I. Zbruyev, V.V. Vashchenko, A.A. Andryushchenko, S.M. Desenko, V.I. Musatov, I.V. Knyazeva, V.A. Chebanov, Synthesis of polyarene derivatives of fused aziridines by Suzuki-Miyaura cross-coupling, Tetrahedron 63 (2007) 4297–4303.

[33] A. Padwa, E. Glazer, Photochemical transformations of small ring heterocyclic compounds. XLII. 1,3-Dipolar cycloaddition reactions of the azomethine ylide derived from the 1,3-diazabicyclo[3.1.0]hex-3-ene system, Journal of Organic Chemistry 38 (1973) 284–288.

[34] H.W. Heine, A.B. Smith III, J.D. Bower, X.V. Aziridines III, Reactions of a 1,3-diazabicyclo-[3.1.0]hex-3-ene with alkenes, alkynes, and diethyl azodicarboxylate, Journal of Organic Chemistry 33 (1968) 1097–1099.

[35] A. Padwa, J. Smolanoff, S.I. Wetmore, Photochemical transformations of small ring heterocyclic compounds. XLV. Photocycloaddition and photodimerization reactions of arylazirines, Journal of Organic Chemistry 38 (1973) 1333–1340.

[36] H. Dürr, Perspectives in photochromism: a novel system based on the 1,5-electrocyclization of heteroanalogous pentadienyl anions, Angewandte Chemie International Edition in English 28 (1989) 413–431.

[37] J. Jin, L. Zou, Efficient one-step synthesis and properties of photochromic diarylethenes having an indene bridging unit, Chinese Journal of Chemistry 29 (2011) 2445–2450.

[38] J. Liu, J. Han, J. Wang, M. Pang, J. Meng, A new biindenylidenedione compound with two azobenzene units: synthesis and photochromic behavior both in solution and in the solid state, Chinese Journal of Chemistry 27 (2009) 1839–1842.

[39] F. Iwahori, S. Hatano, J. Abe, Rational design of a new class of diffusion-inhibited HABI with fast back-reaction, Journal of Physical Organic Chemistry 20 (2007) 857–863.

[40] S. Mitra, N. Tamai, Dynamics of photochromism in salicylideneaniline: a femtosecond spectroscopic study, Physical Chemistry Chemical Physics 5 (2003) 4647–4652.

[41] F. Robert, P. Jacquemin, B. Tinant, Y. Garcia, Trans-keto* form detection in non-photochromic *N*-salicylidene aminomethylpyridines, CrystEngComm 14 (2012) 4396–4406.

[42] J. Harada, Y. Kawazoe, K. Ogawa, Photochromism of spiropyrans and spirooxazines in the solid state: low temperature enhances photocoloration, Chemical Communications 46 (2010) 2593–2595.

[43] O. Godsi, U. Peskin, M. Kapon, E. Natan, Y. Eichen, Site effects in controlling the chemical reactivity in crystals: solid-state photochromism of *N*-(*n*-propyl)nitrospiropyrane, Chemical Communications (2001) 2132–2133.

[44] S.A. Ahmed, Z. Moussa, S.Y. Al-Raqa, S.N. Alamry, Photochromism of Dihydroindolizines part X. Photo-responsive self-assembling organogelators based on photochromic dihydroindolizines and 11-aminoundecanoic acid (AUDA), Journal of Physical Organic Chemistry 22 (2009) 593–606.

[45] J. Cusido, E. Deniz, F.M. Raymo, Fluorescent switches based on photochromic compounds, European Journal of Organic Chemistry (13) (2009) 2031–2045.

[46] S. Mitra, H. Ito, N. Tamai, Transient behavior of 2-(2′,4′-dinitrobenzyl)pyridine photochromism studied by ultrafast laser spectroscopy, Chemical Physics 306 (2004) 185–189.

[47] M. Arvand, M. Moghimi, A. Afshari, N. Mahmoodi, Potentiometric membrane sensor based on 6-(4-nitrophenyl)-2,4-diphenyl-3,5-diaza-bicyclo[3.1.0]hex-2-ene for detection of Sn(II) in real samples, Analytica Chimica Acta 579 (2006) 102.

[48] M.A. Zanjanchi, M. Arvand, A. Islamnezhad, N.O. Mahmoodi, Novel potentiometric membrane sensor based on 6-(4-nitrophenyl)-2-phenyl-4,4-dipropyl-3,5-diazabicyclo-[3,1,0]hex-2-ene for detection of strontium (II) ions at trace levels, Talanta 74 (2007) 125–131.

[49] M.A. Zanjanchi, M. Arvand, N.O. Mahmoodi, A. Islamnezhad, A fast response strontium ion-selective electrode prepared by sol–gel membrane technique, Electroanalysis 21 (2009) 1816–1821.

[50] A. Islamnezhad, N. Mahmoodi, Novel potentiometric Cu^{2+}-selective electrode with subnanomolar detection limit, Desalination 271 (2011) 157–162.

[51] M. Ardon, P.D. Hayes, G. Hogarth, Microwave-assisted reflux in organometallic chemistry: synthesis and structural determination of molybdenum carbonyl complexes. An intermediate-level organometallic-inorganic experiment, Journal of Chemical Education 79 (2002) 1249.

[52] J. Xu, P. Jiao, Direct NH-aziridination of α,β-unsaturated ketones, Journal of the Chemical Society Perkin Transactions 1 (2002) 1491–1493.